All Four Sulfur Isotope Systematics in Mass-Dependent Processes

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We report multiple sulfur isotope ratios ($\delta^{33}S$, $\delta^{34}S$ and $\delta^{36}S$) of IAEA reference materials, modern and Phanerozoic sulfide and sulfate measured by a laser fluorination, dual-gas-chromatographic purification system with a dual inlet isotope ratio mass-spectrometer. Precision and accuracy of the method are evaluated by cross comparison between Geophysical Laboratory and University of Maryland. Our high precision analyses allow us to define natural variations of $\Delta^{33}S$ (= $\delta^{33}S'$-0.515 $\delta^{34}S'$, where $\delta^{x}S' = \ln((^{x}S/^{32}S)_{sample}/(^{x}S/^{32}S)_{ref})\times 1000$) and $\Delta^{36}S$ (= $\delta^{36}S'$-1.9 $\delta^{34}S'$) produced as a result of natural mass-dependent processes.

The observed variations can be explained by the functional differences between the power law of mass-dependent isotope fractionation and the largely linear relationships that govern isotopic mass balance. Small yet measurable non-zero values of $\Delta^{33}S$ and $\Delta^{36}S$ are produced by a combination of processes involving mixing (or branching) and isotope fractionation. Therefore, multi-dimensional sulfur isotope systematics may provide new insights into fundamental aspects of the sulfur biogeochemical cycle for terrestrial mass-dependent processes, including the post-2.0 Ga oceanic sulfate budget and the source of sulfide in the hydrothermal systems.

The mechanism discussed here cannot explain the much larger values of $\Delta^{33}S$ seen in Archean rock records. Furthermore, Phanerozoic samples show a characteristic $\Delta^{33}S$ and $\Delta^{36}S$ relationship that differs from those measured in Archean rocks and laboratory experiments of SO_2 photolysis. Thus, high precision analysis of $\Delta^{33}S$ and $\Delta^{36}S$ may provide a tool to decouple non-zero $\Delta^{33}S$ and $\Delta^{36}S$ produced by mass-dependent processes from those by mass-independent processes in the Archean rocks and meteorites.